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LETTER

Synthesis and photocatalytic activity of mesoporous titania with wormhole-like framework structure consisted of TiO_2(B)

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Introduction

Since the discovery of ordered mesoporous silica materials (e.g. MCM-41) in early 1990s [1–3], they have attracted considerable attention due to their high specific surface area and possible applications as adsorbent, catalyst, optical materials, sensors, and separatory materials [3–5]. A wide range of mesoporous silica materials have been prepared using the structure-directing functions of electrostatic, hydrogen-bonding, and van der Waals interactions. Recently, many efforts have been taken to synthesize ordered mesoporous transition metal oxides for their enormous potential that is not possessed by silica in the fields of electromagnetic, photoelectronics, catalysis, etc. [6–8].

Titanium dioxide (TiO_2) is a really interesting material because of its numerous applications, for example, photocatalysis and catalyst support. There are eight polymorphs of titania [9]. Among them, only anatase and rutile are practical applications, because they are stable under ambient conditions and can be readily synthesized. TiO_2(B), which is one of the titania polymorphs with a layered structure, is also shown to have the photocatalytic activity [10]. In recent years, syntheses of several shaped TiO_2(B) such as nanowires [10], nanoparticles [11], and nanofibers [12] have been reported. However, the obtained TiO_2(B) did not show high photocatalytic activities [10, 11]. On the other hand, mesoporous titania is of considerable interest as it is expected to applications for a high-activity photocatalyst and an electrode material for dye-sensitized solar cells [13, 14]. In recent years, some workers have reported syntheses of mesoporous titania with uniform mesopores having crystalline walls [15–17]. However, the crystalline phase is only anatase and rutile.

In this study, we have firstly succeeded in synthesizing mesoporous titania with uniform mesopores consisted of TiO_2(B) by an evaporation-induced self-assembly (EISA) method. The mesoporous titania shows high photocatalytic activity.

Experimental

1.0 g of Pluronic P-123 was dissolved in 11.0 mL of 1-Butanol. Separately, 1.9 mL of HCl (37 wt%) was added to 2.8 mL of titanium (IV) ethoxide ($Ti(EtO)_4$), followed by stirring for an hour. These surfactant and titanate solutions were combined at room temperature and stirred for 3 h under air atmosphere. The resultant solution was transferred into an open petri dish to form a 1 mm thick liquid layer and then aged at 40 °C in air for 3 days to form gel. During this above experiment process, the temperature was kept constant. After the gel was dried, the as-synthesized sample was calcined in air at 300 °C for 4 h with heating rate of 1 °C/min using a platinum crucible.

The photocatalytic activity of the obtained mesoporous titania sample for oxidative decomposition of acetic acid in aerated aqueous suspension was examined. Prior to the photocatalytic reaction, pre-treatment was carried out to decompose some residual organic matter derived from

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thermal decomposition of surfactant [18]. The sample (50 mg) was suspended in an aqueous solution (5.0 cm^3) containing acetic acid (5.0 vol.%) and was irradiated in the wavelength range from 300 to 700 nm by a 300 W xenon lamp (at room temperature) under air with vigorous magnetic stirring (1000 rpm) for 1 h. After the irradiation, the amount of carbon dioxide (CO_2) in the gas phase was measured by gas chromatograph.

Results and discussion

The obtained as-synthesized sample was transparent yellowish material. The small angle X-ray diffraction (SAXRD) pattern of the calcined sample is presented in Fig. 1. The pattern shows a single broad peak corresponding to a *d* value of 7.7 nm, being suggestive of mesostructural order. The measured *d* spacing is about 30% smaller than that previously reported for mesostructured titania prepared using the same template, P-123 [15, 19]. Figure 2 shows the wide-angle XRD pattern, which is characteristic of TiO_2(B) phase (JCPDS no. 35-0088) without any indication of other crystalline byproducts and the intensity ratios show that the crystallites are randomly oriented. TiO_2(B) is usually derived from by dehydration of hydrogen titanate [20]. Under the present experimental condition, where concentrated HCl is used to hydrolyze the titanium ethoxide, the nucleation process is presumably driven toward the formation of hydrogen titanate, which then lose water and yield a nanocrystalline TiO_2(B) phase by thermal treatment. The broad diffraction peaks are considered to arise from the nano-scale size of the crystals comprising the mesoporous titania sample and their crystallinity.

As shown in the transmission electron micrograph (TEM) image (Fig. 3), the sample has a wormhole-like structure with uniform mesopores [21]. The pore size could be estimated to be around 3 nm, and framework of the material is relatively thick, which is about 4–6 nm. The thick pore wall is helpful for keeping structure from collapsing during calcination [22]. A selected-area electron diffraction (SAED) pattern (Fig. 3 inset) of a sample calcined at 300 °C confirms that these crystallites are indeed TiO_2(B). These results show TiO_2(B) nanocrystallites embedded in the channel wall. The wall thickness is uneven, the unevenness of which is considered to result in the broad diffraction peak of SAXRD pattern.

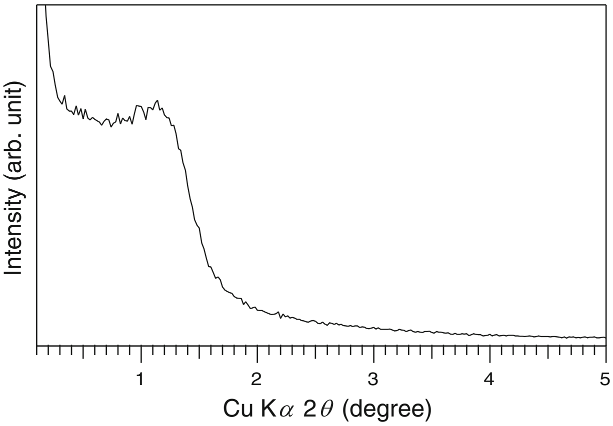

Fig. 1 SAXRD pattern of synthesized mesoporous titania

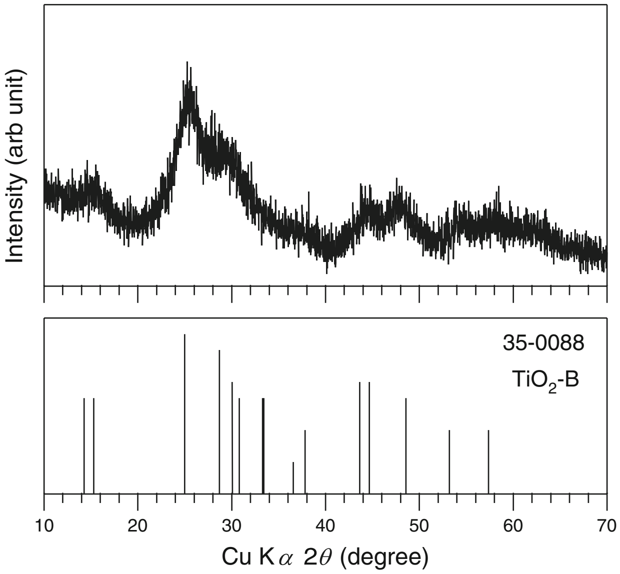

Fig. 2 WAXRD pattern of synthesized mesoporous titania

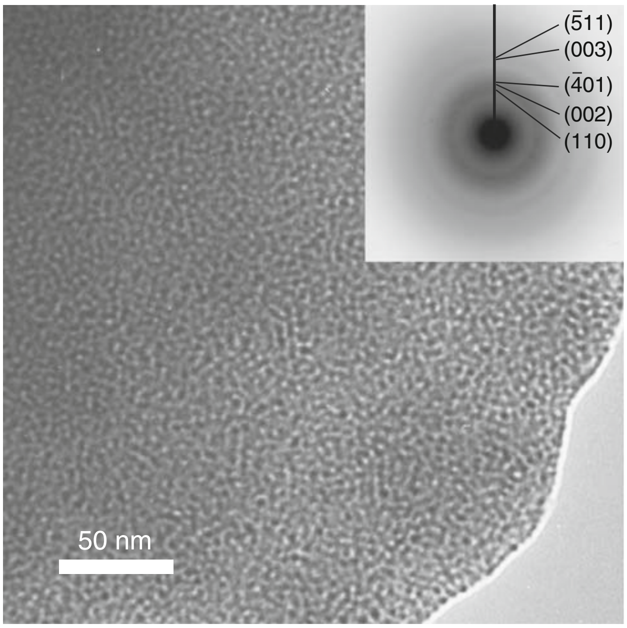

Fig. 3 TEM image of the mesoporous titania and selected-area electron diffraction pattern

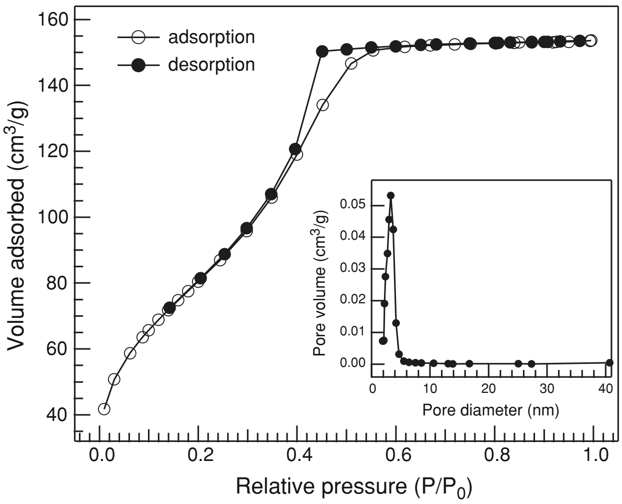

Fig. 4 N_2 adsorption–desorption isotherm for the mesoporous titania. The pore size distribution plot is shown in the inset

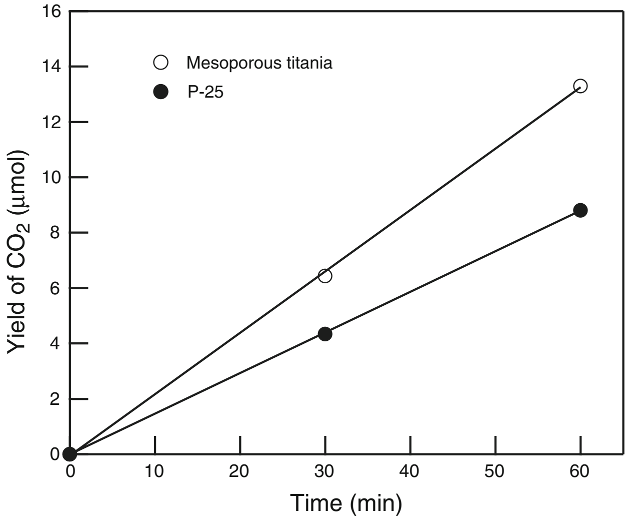

Fig. 5 Time course of CO_2 yield from aqueous acetic acid solution by suspended the mesoporous titania and P-25

The N_2 adsorption–desorption isotherm is shown in Fig. 4. The isotherm could be classified as type IV isotherm characteristic for the mesoporous materials [23]. The Brunauer–Emmett–Teller (BET) surface area was 299 m^2/g. The pore size distribution was determined by Barrett–Joyner–Halenda (BJH) method from the adsorption branch. As shown in the inset in Fig. 4, the average pore size is about 3.0 nm with a narrow size distribution, which is consistent with the TEM image. In the isotherm, obvious adsorption step could be found in relative pressure range of 0.4 to 0.6, which can be ascribed to the capillary condensation of nitrogen molecules in mesopores with a relatively uniform dimension.

In order to evaluate the relative photocatalytic activity of the mesoporous titania, the comparative experiment with Degussa P-25, which has a specific surface area of 50 m^2/g, was carried out. The amount of carbon dioxide produced from the photocatalytic degradation of acetic acid ($CH_3COOH + 2O_2 = 2CO_2 + 2H_2O$) on the mesoporous titania and P-25 was 13.3 and 8.8 μmol, respectively (Fig. 5). It became clear that the mesoporous titania exhibited a 1.5 times higher photocatalytic activity than P-25. Chen et al. reported that the mesoporous titania consisted of both anatase and rutile and was prepared by the same EISA method, which has a specific surface area of 91.6 m^2/g, and it has a 7% higher photocatalytic activity than P-25 for photocatalytic degradation of phenol [14]. In this experiment, the high photocatalytic activity can be attributed to porous structure, large surface area, and nm-order wall thickness. It is well known that porous structure and larger surface area can result in accelerating the reaction rate. And nm-order wall thickness is considered to be favorable for migration of photogenerated electrons and holes to the surface. Therefore, the mesoporous titania had a high photocatalytic activity.

Conclusion

The mesoporous titania with a wormhole-like framework structure was obtained by an evaporation-induced self-assembly method. The walls of the wormhole-like framework were composed of $TiO_2(B)$. The mesoporous titania had a high surface area of 299 m^2/g and an average pore size of about 3.0 nm with a narrow size distribution, and it showed 1.5 times higher photocatalytic activity than P-25 for acetic acid decomposition.

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